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16. ABSTRACT

Particulate samples, collected on Teflon filters by dichotomous samplers in Denver, Colorado, for 12 months during 1979, were analyzed for mass by β radiation attenuation and for elemental composition by x-ray fluorescence. The resulting data were analyzed in terms of a chemical element balance method to resolve particulate mass into the following six components: ammonium sulfate, motor vehicle exhaust, shale, limestone, road salt, and refuse incineration. Time series plots of monthly values revealed that the road salt component was important only during winter and that the motor vehicle exhaust component was substantially elevated during fall and winter. Although the magnitude of the motor vehicle component in the fine particle fraction was elevated during the fall-winter season, its percentage contribution to the total observed mass (∿ 25%) remained reasonably constant throughout the year. The six components plus carbon and nitrate account for almost all of the total particulate mass, although the chemical element balance model underestimated by a factor of 4 the amount of carbon during January. Further mathematical analysis of the data to apportion the carbon more accurately and additional analyses to determine crystalline phases and individual particles are needed and discussed.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution	Dichotomous filter samples	13B
*Aerosols		Q7D
*Weight (mass)		07B
*Chemical elements		

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CHAPTER 2

CHEMICAL ELEMENT BALANCE ANALYSIS OF DENVER AEROSOL

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Since national air quality standards were established by the U.S. Environmental Protection Agency (EPA) (1971), states have had to develop plans to limit the amount of total suspended particulate matter in the atmosphere. Although progress has been made in meeting the standard for particulate matter, the standard is still being exceeded in many areas (EPA, 1977). If further progress is to be made in a cost-effective manner, the magnitude of major emission source components in the mass of ambient aerosol particles must first be known.

Previous investigators have demonstrated the use of a chemical element balance method for resolving the mass of ambient aerosol particles into components from specific sources. To conduct the analysis, the average composition of particles from the major emission sources must be determined and the elemental composition of particles be measured at a receptor site in ambient air.

Miller et al. (1972) used the chemical element balance (CEB) method to determine the abundance of sea salt, soil, automobile emissions and fuel oil fly ash in total suspended particulate matter in Pasadena, California. Several other investigators have applied the method to urban aerosols (Winchester and Nifong, 1971; Friedlander, 1973; Gatz, 1975; Dzubay, 1980). Recently, Kowalczyk et al. (1978) refined the method by using a least-squares mathematical procedure to resolve aerosol mass into source components. Watson (1979) further refined the method by using a properly weighted least-squares procedure.

The present work demonstrates that valuable information can be obtained by applying chemical element balance analysis to X-ray fluorescence (XRF) data on the elemental composition of samples collected in dichotomous samplers. These data were used to resolve size-fractionated aerosol mass into six components: sulfate and related cations, motor vehicle exhaust, shale, limestone, salt and refuse incineration. However, the use of additional analytical and mathematical procedures is proposed to resolve the ambiguities that occurred in the interpretation and determination of such components.

METHODS

Measurements

The results reported here are based on aerosol samples collected during the entire year of 1979 by an automated dichotomous sampler in Denver, Colorado. The sampler was located on top of the National Asthma Center, a one-story building at 21st and Julian Street. The sampler was manufactured by Beckman Instruments, Inc.,* Anaheim, California. It was operated at a flow-rate of 16.7 liters/min and separated particles into fine (<2.5-μm diameter) and coarse (2.5- to ca 15-μm-diameter) size ranges. Particles were collected on 1-μm pore size Teflon®** filters mounted on 5 x 5-cm square frames obtained from Ghia Corporation, Pleasanton, California. The samplers were operated continuously throughout the year. For January through June and for December, the sampling durations were 12 hours and filters were changed at 0700 and 1900 hours, local time. From July through November, the sampling durations were 24 hours and filters were changed at midnight. Samples were shipped for analysis to Research Triangle Park, North Carolina, in containers with padding at least 12 cm thick on all sides to minimize shock and vibration.

*Mention of commercial products or company names does not constitute endorsement by the EPA.

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Samples were analyzed for mass by means of attenuation of β^- radiation in an automated instrument developed by Jaklevic et al. (1980). The radioactive source used was ^{147}Pm. For every 72 samples analyzed, five gravimetrically known mass standards also were analyzed. The instrument calibration was obtained from a least-squares fit of the instrument response to the known standards (Jaklevic et al., 1980).

Samples were analyzed for elemental composition using an XRF spectrometer developed by Jaklevic et al. (1976) and Goulding et al. (1978). The device uses a low-power pulsed X-ray tube and three separate secondary targets to excite the samples and enable detection of a wide range of elements.

The XRF analyzer was calibrated using thin metal films, and X-ray attenuation corrections were made using procedures described by Dzubay and Rickel (1978). A set of six thin foil standards was analyzed for quality assurance. The X-ray spectra were analyzed using a least-squares fitting procedure described by Drane et al. (1980). After the mass and elemental analyses were complete, the samples were analyzed for nitrate and sulfate by ion chromatography using procedures described by Stevens et al. (1978).

Table I indicates typical results of the mass and elemental analysis. The concentrations shown represent monthly averages of the original 12-hour measurements for January and May. The indicated uncertainties represent the average estimated error for the 12-hour measurements and include uncertainties in calibration, attenuation correction, and spectral analysis.

Also shown in Table I are data on total carbon provided by the Lawrence Berkeley Laboratory (Hansen et al., 1979; Rosen and Novakov, 1980). These carbon data were obtained for aerosols collected on quartz fiber filters in a sampler located near our dichotomous sampler. Carbon was analyzed at the Lawrence Berkeley Laboratory by a combustion method accurate to 10% or better (Hansen et al., 1979). The carbon data for January represent the average for 19 days of sampling the fine fraction by means of an upstream Nuclepore filter to remove coarse particles (Cahill et al., 1977). The carbon data for May represent the average for 28 days of sampling particles in a size range corresponding approximately to our combined fine and coarse fractions.

Components in the Chemical Balance

To carry out a chemical element balance analysis, the components must be selected into which the aerosol concentrations are to be resolved. The abundances of all measured elements for each component need to be specified; moreover, the specified abundances should accurately represent the composition of the particulate matter as it exists in the collected samples. The accuracy of the results of the chemical element balance analysis depends on the accuracy with which the components are known.

Table I. Monthly Averages of Aerosol Mass and Elemental Concentrations in ng/m^3 in the Fine and Coarse Particulate Fractions in Denver during January and May, 1980[a]

Element	January		May		Uncertainties[b]	
	Fine	Coarse	Fine	Coarse	Fine	Coarse
Mass	26,000	27,100	9,800	16,100	2,700	2,700
C	17,000[c]		[c,d]	[c,d]		
NO_3^-	1,740	170	20	29		
Al	-13	1,351	52	904	28	125
Si	171	4,213	154	3,322	21	521
P	61	101	-4	34	7	13
S	1,065	297	557	161	50	76
Cl	241	1,761	18	83	5	21
K	58	571	42	453	3	63
Ca	57	571	51	601	4	66
Ti	-1	80	-7	56	7	14
V	0	1	2	4	4	5
Cr	6	3	6	5	3	3
Mn	5	18	11	18	2	3
Fe	33	684	72	636	5	52
Ni	3	1	0	1	1	1
Cu	10	0	7	3	2	2
Zn	26	27	14	20	2	3
As	35	7	-7	-3	3	2
Se	1	0	0	0	0.5	0.5
Br	350	95	102	42	6	3
Rb	-2	1	1	2	1	1
Sr	1	9	1	5	0.5	1
Cd	0	0	1	15	1	2
Sn	2	0	2	1	1	1
Sb	1	0	1	0	1	2
Pb	1,001	305	417	137	23	11

[a] Negative numbers are not suppressed. Note large uncertainties when negative numbers occur.
[b] Average uncertainties in the 12-hour May data. See text.
[c] From Rosen and Novakov (1980) and Hansen et al. (1979).
[d] The total carbon for the combined fractions is 7200 ng/m^3.

We attempted to describe the Denver aerosol in terms of the following six components: sulfate and related cations, motor vehicle exhaust, shale, limestone, salt and refuse incineration. Their compositions are given in Table II. The rationale for selecting these components is described below.

Table II. Composition in mg/g of the Six Components Used in Chemical Element Balance Analysis Applied to Dichotomous Sampler Data

Element	Ammonia Sulfate	Motor Vehicle	Shale	Limestone	Salt	Refuse
C		563	15	114		
Na			9.6	0.4	325	82
Mg		6	15	47	39	13
Al			80	4.2		14
Si*[a]			273	24		48
P		0.9	0.7	0.4		
S*	242	6	2.4	1.2		27
Cl*		19	0.18	0.15	582	200
K			26.6	2.7		12
Ca*			22.1	302	12	17
Ti			4.6	0.4		2.4
V			0.13	0.02		
Cr			0.09	0.01		0.5
Mn		0.6	0.85	1.1		0.7
Fe*		1	47.2 (9.4)[b]	3.8		6.5
Ni			0.07	0.02		
Cu			0.05			1.7
Zn*		3	0.1	0.02		120
Se						
Br*		43 (17)[b]		0.01	2	1.5
Rb			0.14			
Sr			0.3	0.61		
Cd						1.5
Sn*			0.01			11.5
Sb						2.1
Ba		0.9	0.58	0.01		0.7
Pb*		148	0.02	0.01		81
Other[c]	758	215	501	498	2	396
Total	1000	1000.7	999.7	1000.1	1000	1000

[a] The asterisk indicates the elements used in least-squares fit.
[b] The numbers in parentheses are used in Equation 4 to represent σ_a.
[c] Includes H, N and O.

Sulfate Component

Stevens et al. (1978) found that when precautions were taken to prevent neutralization by ammonia, the sulfur in fine particles occurred as mixtures of sulfuric acid and ammonium sulfate. However, in the present experiment no attempt was made to prevent neutralization, which from our previous

experience results in such mixtures becoming entirely ammonium sulfate during normal sample handling. Thus, we assume that at the time of analysis the sulfur was in the form of ammonium sulfate and its sulfur abundance was 242 mg/g, as indicated in Table II. We did not attempt to attribute the sulfur to a specific source. According to Wilson (1978), atmospheric sulfate can be due not only to direct emissions, but also to secondary processes in the atmosphere. Both local sources and transport from distant sources can be important.

Although the chemical form of particulate sulfur in the coarse fraction is not well known, the ammonium sulfate component was also used to represent the sulfur in that fraction. If coarse particle sulfur were actually in another chemical form, the resulting error would be negligible due to the low abundance of sulfur in the coarse fraction.

Motor Vehicle Component

The composition of this component is based on primary particulate emission rates for cars and trucks measured in highway tunnels by Pierson (1978, 1979). The emission rates are weighted, assuming that cars and diesel-powered trucks account for 96% and 4% of the traffic, respectively. An emission rate of 10 mg/km was assumed for lead. The magnitude of the motor vehicle component is determined by bromine and lead concentrations in the collected aerosol. In Denver, the ratios of the monthly averages of lead and bromine had a seasonal variation. Figure 1 indicates that the ratio decreased monotonically from 0.35 in January to 0.23 in July and then rose monotonically to 0.33 in December. Because of the instability of bromine on auto exhaust particles (Winchester et al., 1967; Eldred et al., 1978), we used an average bromine:lead ratio of 0.29 ± 0.11, rather than the value 0.39 for fresh auto exhaust. Because of (1) possible variations in the relative amounts of car and diesel truck traffic, (2) possible differences in the exhaust particle composition from what we assumed for the component, and (3) possible secondary aerosol formed from vehicle exhaust gases, we estimate the accuracy of the deduced motor vehicle component mass concentration to be about ±50%.

Crustal Components

Detailed multielement data on crustal matter emissions from soil in the Denver area were not available to serve as bases for the crustal components. Even if such data were available, their applicability is unclear because of the multitude of possible sources of crustal matter shown in Table III. Gatz (1978) and Dzubay (1980) have shown that both a silicon-rich and a calcium-

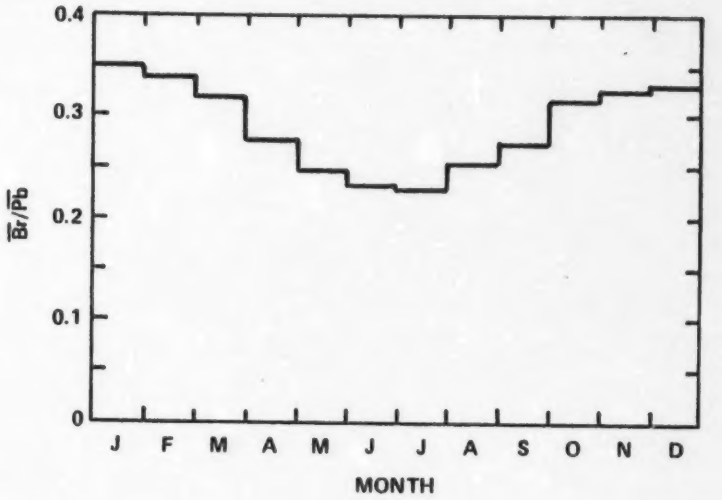

Figure 1. Ratios of average monthly bromine and lead concentrations in Denver during 1979.

Table III. Sources of Crustal Matter That Can Contribute to Shale and Limestone Components

Category	Subcategory
Transportation	Unpaved roads
	Road shoulders
	Paved roads
	Winter road sanding
Wind Erosion	Agriculture
	Other fields
Earthmoving	Agriculture
	Construction
Combustion	Coal
	Refuse
	Oil
Manufacturing	Cement
	Steel
	Many others
Quarrying	Earthmoving
	Processing
	Shipping

rich crustal component were needed to represent the crustal matter in St. Louis by two types of sedimentary rocks: shale and limestone. We used the same components to represent the crustal matter in Denver aerosol. Their compositions are shown in Table II and are taken from Tables 6.1 and 6.5 of the book entitled *Principles of Geochemistry* (Mason, 1966).

Salt Component

An inspection of our Denver aerosol data (see Table I for example) indicates a high chlorine concentration in the coarse particle fraction during the winter months, presumably due to the application and resuspension of salt used for snow removal on streets. No strong association of the chlorine with other elements detectable by XRF was evident. For example, there was neither evidence for a wintertime increase in calcium, nor a strong correlation between calcium and chlorine. However, the chlorine may associate with sodium, which cannot be determined by our XRF analyzer. The composition of the salt component shown in Table II is that of sea salt (Weast, 1976).

Refuse Component

Greenberg et al. (1978) demonstrated that municipal incinerator emissions are fairly uniform in composition for both Washington, DC, and Chicago, Illinois. Their average composition is listed in Table II as the refuse component. The magnitude of this component is determined by the zinc concentrations. If refuse incineration were not the only major source of zinc, then failure to include the other sources would cause the magnitude of the refuse component to be overestimated.

Procedure for Determining the Components

A basic assumption made in using the chemical element balance method is that the aerosol composition can be represented as:

$$P_k = \sum_j a_{jk} M_j \qquad (1)$$

where P_k = the predicted concentration of element k,
a_{jk} = the fractional abundance of element k in component j,
M_j = the total mass concentration of component j.

The sum is carried out for all components j.

The fractional abundances for any component j must be normalized so that

$$\sum_k a_{jk} = 1 \qquad (2)$$

where the sum over k is carried out for all elements capable of contributing mass to the aerosol. The component arrays in Table II satisfy this condition.

The component concentrations M_j are obtained by the technique of linear least-squares (Bevington, 1969), in which χ^2 is minimized in the expression

$$\chi^2 = \Sigma (O_k - P_k)^2 / \sigma_k^2 \qquad (3)$$

where O_k is the observed concentration of element k and σ_k is a weighting factor given by

$$\sigma_k^2 = \sigma_{O_k}^2 + \Sigma \sigma_{a_{jk}}^2 M_j^2 \qquad (4)$$

The weighting factor given in Equation 4 was first used in CEB analysis by Watson (1979). Its unique feature is that it includes not only the uncertainties in the elemental concentrations σ_O, but also uncertainties σ_a in the elemental concentrations in the components. The uncertainties defined and illustrated for Table I were used as σ_O. Because of incomplete information on uncertainty in the component compositions, nonzero values of σ_a were used only for bromine in the motor vehicle component and iron in the shale component (see Table II).

The solution to Equations 3 and 4 was carried out in three iterations. In the first iteration, weights σ_O were calculated using $M_j = 0$. In the next two iterations they were calculated using the values of M_j from the previous iterations. The sum in Equation 3 is carried out only for those elements k for which a fit to the data is demanded, which in the present work only includes the following nine elements: Si, S, Cl, Ca, Fe, Zn, Br, Sn and Pb. The weighting factors σ_k for those elements obtained after the third iteration are shown in Tables IV and V.

The total suspended particulate mass concentration in each size fraction is estimated from the following equation:

$$M = \sum_j M_j + \sum_k (O_k - P_k) \qquad (5)$$

where the first sum is carried out for all components and the second is a sum for all measured elements except for the nine used in the least-squares fit. The second term is needed to account for measured elements that are not well predicted in the components.

Table IV. A Comparison of Observed and Predicted Elemental and Total Mass Concentrations for the Average January Fine Particulate Denver Data[a]

Element	σ	Total Observed	Total Predicted	Ammonium Sulfate	Motor Vehicle	Shale	Limestone	Salt	Refuse
C		17,000	3,811	0	3,787	9	15	0	0
NO_3^-		1,740							
Na		[b]	103	0	0	6	0	92	5
Mg		[b]	68	0	42	9	6	11	1
Al		-13	49	0	0	47	1	0	1
Si*	26	171	167	0	0	161	3	0	3
P		61	7	0	6	0	0	0	0
S*	72	1,065	1,065	1,014	42	1	0	8	0
Cl*	17	241	241	0	62	0	0	166	13
K		58	19	0	0	16	0	3	0
Ca*	4	57	57	0	0	13	39	3	1
Ti		-1	3	0	0	3	0	0	0
V		0	0	0	0	0	0	0	0
Cr		6	0	0	0	0	0	0	0
Mn		5	5	0	4	1	0	0	0
Fe*	8	33	35	0	7	28	0	0	0
Ni		3	0	0	0	0	0	0	0
Cu		10	0	0	0	0	0	0	0
Zn*	2	26	26	0	18	0	0	0	8
As		35	0	0	0	0	0	0	0
Se		1	0	0	0	0	0	0	0
Br*	114	350	286	0	286	0	0	1	0
Rb		-2	0	0	0	0	0	0	0
Sr		1	0	0	0	0	0	0	0
Cd		0	0	0	0	0	0	0	0
Sn*	2	2	1	0	0	0	0	0	1
Sb		1	0	0	0	0	0	0	0
Pb*	55	1,001	1,003	0	998	0	0	0	5
Other[d]			5,002	3,170	1,447	295	65	0	26
Mass		26,500	27,070[e]	4,184	6,703	588	130	284	65

[a] In units of ng/m³.
[b] Not measured.
[c] The asterisk indicates elements included in the least-squares fit.
[d] Mainly includes N and O other than NO_3^- and H.
[e] Includes excess carbon.

Table V. A Comparison of Observed and Predicted Elemental and Total Mass Concentrations for the Average January Coarse Particulate Denver Data[a]

Element	σ	Total Observed	Total Predicted	Ammonium Sulfate	Motor Vehicle	Shale	Limestone	Salt	Refuse
C		[b]	1,422	0	1,118	223	78	3	0
NO_3^-		170							
Na		[b]	1,106	0	0	141	0	953	13
Mg		[b]	381	0	12	220	32	115	2
Al		1,351	1,177	0	0	1,172	3	0	2
Si*	1,350	4,213	4,023	0	0	3,998	17	1	7
P		101	12	0	2	10	0	0	0
S*	162	297	297	169	12	35	1	80	0
Cl*	523	1,761	1,765	0	18	3	0	1,713	31
K		571	426	0	0	390	2	34	0
Ca*	86	571	571	0	0	324	209	36	3
Ti		80	68	0	0	67	0	0	0
V		1	2	0	0	2	0	0	0
Cr		3	1	0	0	1	0	0	0
Mn		18	15	0	1	12	1	0	0
Fe*	148	684	697	0	2	691	3	0	1
Ni		1	1	0	0	1	0	0	0
Cu		0	1	0	0	1	0	0	0
Zn*	3	27	25	0	5	1	0	0	18
As		7	0	0	0	0	0	0	0
Se		0	0	0	0	0	0	0	0
Br*	34	95	91	0	84	0	0	6	0
Rb		1	2	0	0	2	0	0	0
Sr		9	6	0	0	4	0	1	0
Cd		0	0	0	0	0	0	0	0
Sn*	1	0	2	0	0	0	0	0	2
Sb		0	0	0	0	0	0	0	0
Pb*	23	305	307	0	295	0	0	0	12
Other[d]			8,698	529	428	7,338	344	1	61
Mass		27,100	21,590	697	1,980	14,645	690	2,942	154

[a] In units of ng/m³.
[b] Not measured.
[c] The asterisk indicates elements included in the least-squares fit.
[d] Mainly includes N and O other than NO_3^- and H.

RESULTS

Tables IV and V illustrate results of the computations. The columns pertaining to each component contain values of the products $a_{ik}M_j$ and represent the estimated elemental concentrations contributed by each component. At the bottom of each column is listed the estimated value of M_j, the total component mass concentration. The column labeled "Total Observed" represents the measured elemental and mass concentrations from Table I. The elemental concentrations in the column labeled "Total Predicted" are values calculated using Equation 1. The total predicted mass was calculated from Equation 5.

According to Tables IV and V, good agreement exists between the observed and predicted values for total mass and for the nine elements used in the least-squares fit. Although concentrations of trace elements such as potassium, chromium, nickel and copper are not predicted accurately, their total concentrations are very low. The differences between predicted and observed values for aluminum and phosphorus probably are due to imprecision in the observations. In the case of carbon, which is the most abundant observed species, the model fails badly by underpredicting the concentration by more than a factor of 4.

Figure 2 illustrates monthly averages for January and May 1979 of size-fractionated Denver aerosol percentage composition. As noted above, excellent agreement was found between the sum of the component concentrations and the observed mass concentration for the fine fraction data for January. The component labeled (T) represents trace element concentrations exclusive of carbon and nitrate from the second sum in Equation 5. The component labeled "excess carbon" represents the difference between observed and predicted amounts of carbon. Data on carbon in the coarse fraction were not available for January. Some or all of the component labeled with an asterisk (*) could be due to excess carbon.

No data on size-fractionated carbon are available for the month of May, but total carbon for the combined size fractions was measured to be 7.2 $\mu g/m^3$. The following argument shows how the excess carbon can account for the component labeled with asterisks (*) in Figure 2: the chemical element balance calculation for May predicts 2.4 $\mu g/m^3$ carbon (1.6 and 0.8 $\mu g/m^3$ in the fine and coarse fractions, respectively). Thus, for total carbon in the combined fractions the excess carbon (observed-predicted) is 4.8 $\mu g/m^3$. In the fine and coarse fractions, the components labeled by asterisks (*) amount to 3.9 and 0.5 $\mu g/m^3$, respectively, and their total is 4.4 $\mu g/m^3$. Since the latter is in good agreement with the 4.8 $\mu g/m^3$ excess carbon, the components labeled with asterisks (*) are likely to consist of excess carbon.

Figures 3 and 4 are time-series plots of monthly values of the components deduced in the chemical element balance analysis. The motor vehicle component had substantially elevated concentrations during the fall and winter months. The salt component was sharply elevated during January, February and December and had negligible values during late spring, summer and early fall. These components may account for part of Denver's late fall and winter elevated aerosol concentrations, as described by Russell (1976). The shale and sulfate components were also elevated during the fall and winter; however, the effect was less pronounced for them than for the salt and motor vehicle components. In the coarse fraction, the limestone component was only 5% as large as the shale component, which is very small compared to the situation in St. Louis for which the limestone component was 50% as large as the shale component (Dzubay, 1980).

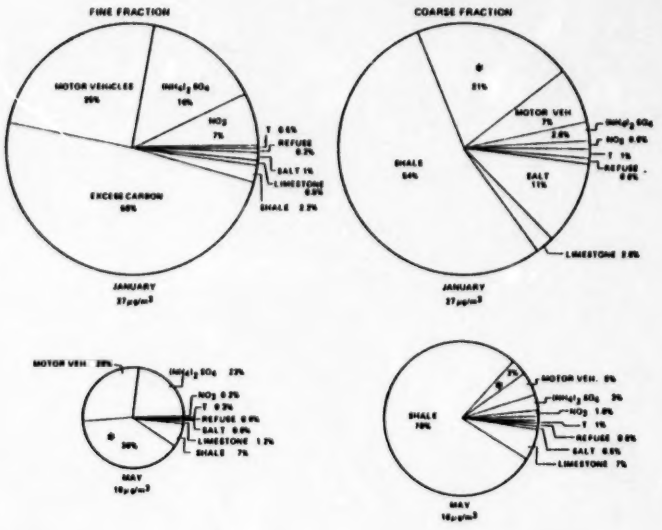

Figure 2. Monthly averages of size-fractionated Denver aerosol mass and composition for January and May, 1979. The components labeled by (*) and (T) are discussed in the text.

DISCUSSION

While we can account for the observed mass in terms of Equation 5, some ambiguities remain. One serious ambiguity concerns carbon. Although Table IV indicates that carbon is the most abundant element in the fine fraction,

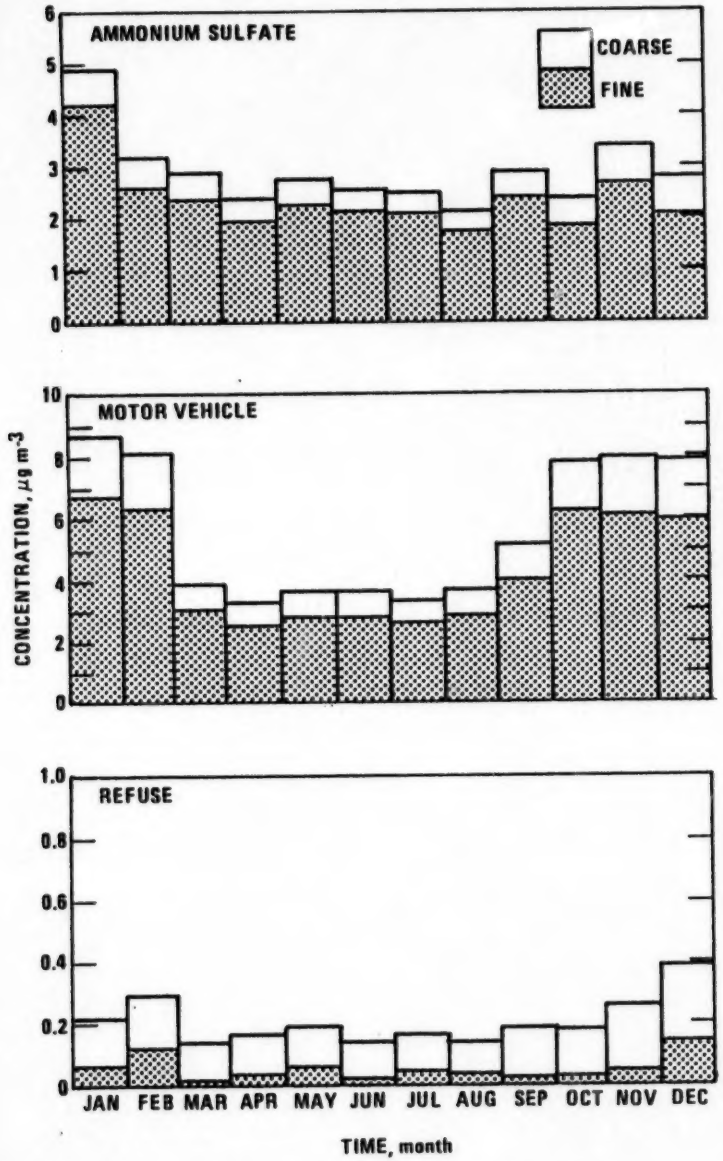

Figure 3. Monthly values of ammonium sulfate, motor vehicle and refuse components in Denver during 1979.

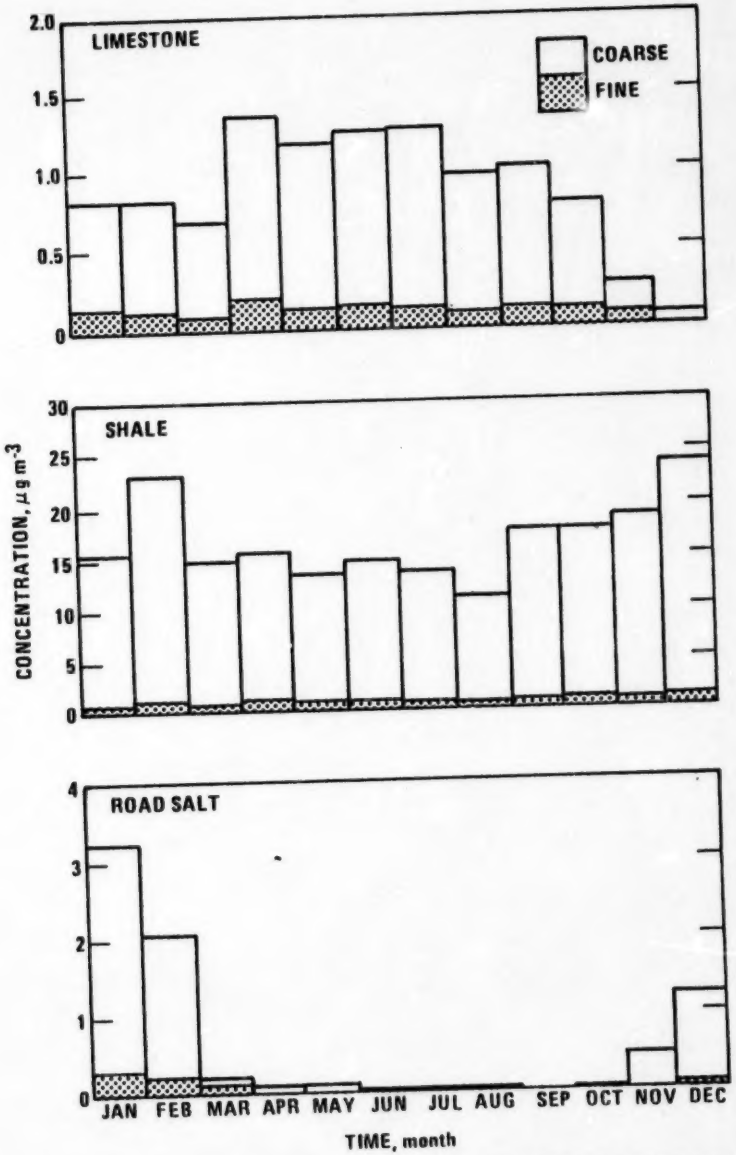

Figure 4. Monthly values of limestone, shale and road salt components in Denver aerosol during 1979.

the chemical element balance model only accounts for 22%. The total observed fine fraction mass is accounted for only because the second sum in Equation 5 includes the 78% of carbon that is not resolved into our six components. The reason for our failure to resolve all of the carbon may be due partly to an incorrect composition of our motor vehicle component. The composition that we used was based on vehicle emissions at low elevations, which may be inappropriate for vehicles operated in Denver's rarefied air at a 1600-meter elevation. Also, the data were based on emissions from automobiles, which did not use significant amounts of unleaded gasoline.

Additional sources of the unresolved carbon are expected to be particles from oil, natural gas and wood combustion for space heating. Heisler et al. (1980) inferred that for Denver during November and December of 1978, total particulate emissions due to natural gas combustion for space heating were nearly as high as those due to automobiles. The amount of particulate carbon from wood combustion in fireplaces and stoves can be estimated from potassium in the aerosol. According to Cooper et al. (1979), potassium constitutes about 0.8% of wood smoke, and the carbon:potassium ratio is about 70. An examination of our monthly averaged data indicates that potassium concentrations in the fine fraction were about 10–15 ng/m^3 higher in winter than in summer. Thus, wood burning can contribute about 1 μg/m^3 to the average monthly carbon, which is about 6% of the total average carbon. Courtney et al. (1980) evaluated an eight-hour evening episode on December 17, 1978, for which the mass concentration of the wood smoke component was estimated to be 33 μg/m^3.

A disadvantage of the chemical element balance method as used in the present work is that independent information is required on the number of major components and their compositions. In the case of carbon, our information appears to be inadequate. However, Hopke et al. (1980) and Alpert and Hopke (1980) have developed a mathematical procedure that may overcome this problem. Rather than average samples together as in the present work, they apply a modified form of factor analysis to the set of all samples in such a way that the number of components, their average composition and their average magnitudes can be determined. Application of this new method to the Denver data may prove useful.

The origins of our shale and limestone components were not defined and constitute another ambiguity. To develop cost-effective air quality implementation plans, the shale and limestone components need to be resolved into at least as many categories as shown in Table III. To accomplish this, additional analytical procedures are needed to supplement the elemental data obtained by XRF. Davis and Johnson (1980) have applied X-ray diffraction (XRD) analysis to particulate samples in Rapid City, South Dakota, and were able to apportion major crystalline species to specific sources. Also, the use of automated scanning electron microscopy (SEM) can be valuable both in identifying individual particles and in estimating quantitative amounts of each particle type (Lee et al., 1979). Comparability tests need to be conducted to demonstrate that equivalent results on the major elemental species can be deduced from XRF, XRD and SEM data.

SUMMARY

Particulate samples were collected on Teflon filters in dichotomous samples in Denver, Colorado, for 12 months during 1979 and analyzed for mass by β^- radiation attenuation and for elemental composition by X-ray fluorescence. The resulting data were analyzed in terms of a chemical element balance method to resolve particulate mass into the following six components: ammonium sulfate, motor vehicle exhaust, shale, limestone, road salt and refuse incineration. Time-series plots of monthly values reveal that the road salt component was important only during winter, and that the motor vehicle exhaust component was substantially elevated during fall and winter. However, while the magnitude of the motor vehicle component in the fine fraction was elevated during the fall-winter season, its percentage contribution to the total observed mass ($\sim$25%) remained reasonably constant throughout the year. The seasonal variability of the magnitude reflects the well-known seasonality of the meteorological dispersion factor for Denver (Russell, 1976), rather than a variability of the source emissions. The six components, plus carbon and nitrate, account for almost all of the total particulate mass, although the chemical element balance model did underestimate by a factor of 4 the amount of carbon during January. Further mathematical analysis of the data will be needed to apportion the carbon more accurately. Further analysis to determine crystalline phases and to identify individual particles will be needed to apportion the mass of the shale and limestone components into subcategories of interest for developing air quality implementation plans.

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